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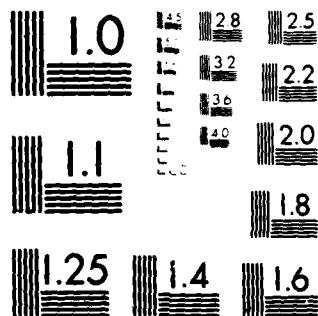UNCLASSIFIED   TR-3   NL

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TECHNICAL REPORT NO. 3

THEORETICAL MODELS FOR THE ELECTRONIC STRUCTURE OF HYDROGENATED

AMORPHOUS SILICON II: THREE-CENTER BONDS

by

M. E. Eberhart, K. H. Johnson, and D. Adler

Center for Materials Science and Engineering

Massachusetts Institute of Technology

Cambridge, MA   02139

March 31, 1982

ABSTRACT

SCF-$X\alpha$-SW molecular-orbital calculations have been carried out for several configurations of hydrogenated silicon clusters in order to determine the contribution of three-center bonding to the electronic structure of hydrogenated amorphous silicon. Three-center bonding of dissociated molecular hydrogen is shown to stabilize Si-Si bonds over a wide range of Si-Si distances. It can be concluded that hydrogenation can in principle, saturate all strained as well as dangling bonds in a-Si. The results further indicate that a single hydrogen three-center bond is unlikely in a-Si:H alloys.

I. Introduction

The discovery that a-Si:H alloys can be doped either n-type or p-type[1] and can be used as the active material in high-efficiency solar cells[2] has stimulated a great deal of interest in the electronic structure of these semiconductors. Despite this enormous interest, however, many unanswered questions remain.[3,4]

It is clear that pure a-Si contains large defect concentrations including both strained and dangling bonds, and that both of these are compensated by the addition of hydrogen. Sol et al.[5] have shown that a-Si deposited via the thermal decomposition of SiH_4 contains the order of 10^{19} unpaired spins $/cm^3$, but that these are eliminated by introducing approximately the same concentration of hydrogen. Furthermore, they were able to incorporate over 100 times more hydrogen into such films after removal of the unpaired spins. This is strong evidence that spinless defects are present in a-Si films. Further evidence comes from effusion experiments which indicate that about 100 times as much hydrogen is given off than unpaired spins are created.[6]

There are several possible explanations of the spinless defects. The most straightforward of these is simply an array of strained bonds, either with stretched distances or distorted bond angles. Other possibilities include charged pairs of dangling bonds,[7,8] doubly coordinated silicon atoms,[9] or three-center bonds with a negative correlation energy.[10] These proposed defects have very different electronic structures, which might allow for an experimental determination of their concentrations. Strained bonds would be expected to yield valence and conduction band tails, doubly coordinated silicon centers should provide two different EPR lines upon n and p doping, and negatively correlated defects should tend to pin the Fermi energy. However, at present, no experiments have been carried out which can unambiguously eliminate any of the proposed spinless defects.

In a previous paper,[11] the results of self-consistent-field $X\alpha$ scattered-wave (SCF-$X\alpha$-SW) molecular-orbital calculations on silane molecules and silicon-hydrogen clusters demonstrated that such clusters serve as models for the local electronic structure of a-Si:H alloys. However, the clusters investigated only contained terminal hydrogen atoms. In this paper, we present the results of SCF-$X\alpha$-SW calculations on clusters containing three-center bonds. The results of these calculations are presented in Section II. In Section III, we discuss the insights that these results yield with regard to the electronic structure of a-Si:H alloys.

II. Results

Before an evaluation of three-center bonding in a-Si:H is possible, we must model the Si-Si bond in these alloys. In order to do this, we use the cluster Si_2X_6 where X represents a saturator; Si_2H_6 is an disilane-like molecule saturated by six hydrogen atoms at a Si-H distance equal to the crystalline Si-Si nearest-neighbor separation of 2.35Å. If such a cluster is to serve as a good model for the Si-Si bond in a-Si:H, the molecular-orbital energy levels should be insensitive to the conformation of the saturators yet highly sensitive to the Si-Si distance. In order to test the model, we calculated the molecular-orbital energy levels for both the eclipsed and staggered conformations of the saturators with the Si-Si distance being held at 2.35Å, and then recalculated the energy levels using a staggered cluster with a varying Si-Si distance. The results are shown in Fig. 1. It is clear from a comparison of Fig. 1(a) and 1(b) that the energy levels are completely insensitive to the saturator conformation, while Fig. 1(c) strikingly shows their extreme sensitivity to a changing Si-Si bond length. A separate calculation demonstrates that an increase of the Si-saturator bond length parallels the behavior of an increasing Si-Si bond length. Thus, these clusters serve as good models for the Si-Si bond

in tetrahedrally coordinated a-Si alloys.

Since we are modeling only the Si-Si bond rather than the local atomic configuration, we can restrict our attention to those molecular orbitals that have appreciable electronic density in the region between the silicon atoms. These are indicated in Fig. 1 by solid lines (The molecular orbitals corresponding to the dotted lines are primarily located near the saturators.). Four molecular orbitals are thus of interest. The lowest-lying is gerade and is composed predominantly of silicon 3s orbitals. Since the energy of this orbital is independent of the Si-Si bond length, it is nonbonding. The next-lowest-lying molecular orbital is ungerade, but is also composed predominantly of silicon 3s orbitals and is nonbonding. The other two are the Si-Si bonding and antibonding orbitals. It is clear from Fig. 1 that for Si-Si separations larger than the crystalline value of 2.35Å these can have energies within the band gap. When the Si-Si distance is less than 3.1Å, the bonding orbital is occupied and the antibonding orbital is empty, resulting in weak bonds. Alternatively, for Si-Si separations greater than 3.1Å, the antibonding orbital is the occupied one, yielding dangling bonds.

It is generally assumed that hydrogenation of pure a-Si results in the saturation of the dangling Si-Si bonds via the dissociation of molecular hydrogen to form two Si-H bonds. This process is sketched in Fig. 2. The H-H bonding orbital mixes with the Si-Si gerade orbitals to form type 1 and type 3 molecular orbitals, while the H-H antibonding orbital mixes with the Si-Si ungerade orbitals to form type 2 and type 4 molecular orbitals. The relative energies of these molecular orbitals depends on the fraction of nonbonding character in the original orbitals, in turn a sensitive function of the interatomic distances. Fig. 3 shows the energies of the molecular orbitals which arise from the dissociation of a hydrogen molecule to saturate the dangling bonds

of a pair of silicon atoms 3.2Å apart. The H-H bonding orbital mixes with
the unoccupied Si-Si bonding orbital, yielding a low-lying type 1 molecular
orbital which tends to widen the valence band of the a-Si. The second-lowest-
lying molecular orbital is type 4 and results from the mixing of the ungerade
Si-Si nonbonding and the H-H antibonding orbitals. The gerade Si-Si nonbonding
orbital and the H-H bonding orbital mix to produce a type 3 molecular orbital.
Finally, the Si-Si antibonding orbital mixes with the H-H antibonding orbital,
yielding a type 2 molecular orbital. The overall result is the occupation
of two H-H bonding and two H-H antibonding orbitals, yielding a nonbonding H-H
interaction, but simultaneously inducing a strongly bonding Si-H interaction.
Contour plots of the four molecular orbitals are shown in Figs. 4 through 7. It is clear
that these results are consistent with the idea of hydrogen saturating the
dangling bonds of pure a-Si.

For Si-Si separations less than 3.1Å, it might appear that there is
insufficient room to insert a hydrogen molecule between the Si-Si bond. However,
since the hydrogen orbitals are of s character, they are insensitive to the
angular position of the atoms. In fact, by rotating the hydrogen atoms off
the Si-Si axis, thus varying the Si-H-H bond angle, the equilibrium Si-H and
H-H bond lengths can be preserved over a wide range of Si-Si distances. The
molecular-orbital levels for fixed Si-H separations of 1.35Å and H-H separations
of 0.8Å is shown in Fig. 8 as the Si-Si distance varies from 3.4Å to 2.5Å. At
all Si-Si separations, the introduction of hydrogen stabilizes the orbitals that
would lie in the band gap in pure a-Si. Thus, hydrogen can compensate stretched
as well as dangling bonds in a-Si.

A contour plot of a stabilized bonding orbital for a Si-Si separation
of 3.2Å is given in Fig. 9. The stabilization results from increased bonding
between the silicon atoms and the more distant hydrogen atoms, i.e. increased

three-center-bonding activity. Note that when the hydrogen atoms are not located along the Si-Si axis, at least two completely equivalent positions exist for them, and we should expect rapid oscillations between these equivalent conformations.

Fisch and Licciardello[10] suggested that a single hydrogen atom could bridge between two silicon atoms in a-Si:H, and they identified two occupied molecular orbitals with appreciable electron density in the region between the two silicons. In Fig. 10, we show the molecular orbital levels which would result from a single hydrogen atom between two silicon atoms 3.2Å apart. Clearly, four rather than two molecular orbitals are important. The lowest-lying is bonding between both silicons and the hydrogen atom via the Si 3s orbitals. The second-lowest-lying is bonding between the hydrogen atom and the nearest silicon atom but weakly antibonding between the two silicon atoms (When the hydrogen atom is half-way between the two silicons, this molecular orbital is Si-H nonbonding). The third-lowest-lying molecular orbital is bonding between both silicon atoms and the hydrogen atom via the Si 3p orbitals. Finally, the highest-lying occupied molecular orbital is antibonding between the silicon atoms and nonbonding between the hydrogen atom and both silicon atoms when the hydrogen is half-way between the two silicons. However, if the hydrogen atom is displaced toward either silicon atom, this molecular orbital remains anti-bonding between the silicons but becomes bonding between the hydrogen atom and the nearer silicon atom. This additional bonding interaction stabilizes the asymmetric displacement of the hydrogen.

III. Discussion

The molecular-orbital stabilization described at the end of Section II has been interpreted[10] as leading to a negative effective correlation energy for the Si-H-Si defect center in a Si:H However, the existence of a negative

effective correlation energy requires that the energy to place a second electron in the molecular orbital be lower than that of the first. Our results suggest that even if the molecular orbital is singly occupied the hydrogen atom is displaced from the center because of the increased bonding interactions. This stabilization has nothing to do with a negative effective correlation energy. Although doubly occupying the molecular orbital may result in an additional stabilization from an increase in the "hydrogen bonding" contribution, it would appear unlikely that this could overcome the extra repulsion from the presence of two electrons in the same orbital. In any event, the much greater stabilization from the presence of two hydrogen atoms between the separated silicon atoms should lead to a negligibly small density of the single-hydrogen centers, particularly in view of the fact that film growth in a-Si:H almost certainly takes place primarily via SiH_2 reactions.[12] In fact, the concerted cleavage of hydrogen molecules to form metal-hydrogen bonds, as exemplified by the process sketched in Fig. 3, is common in many homogeneous catalytic processes.[13] All of these homogeneous processes require that the metal expand its valence shell. It is well known that silicon reacts almost exclusively by expanding its valence shell and passing through a transition state of the type shown in Fig. 3.[14] This, coupled with the fact that the concerted addition of hydrogen molecules can stabilize Si-Si bonds over a wide range of Si-Si separations, supports the conjecture that three-center bonds in a-Si:H alloys almost exclusively involve hydrogen molecules rather than individual atoms.

The possibility of significant densities of three-center bonds of the type described here has not heretofore been considered in a-Si:H alloys.[15] A major consequence of our results is that stretched bonds can be compensated by hydrogen removing states from the valence and conduction band tails. This

is consistent with the sharp absorption edges observed in a-Si:H alloys.[16] It further suggest that mechanisms other than the breaking of stretched bonds[17] be sought to account for the observed photo-induced changes[18] which characterize these materials.

Three-center bonds could well be the origin of one of the peaks observed in hydrogen effusion studies.[19] The residual bonding component after release of a hydrogen molecule from the centers considered here suggest that effusion can occur at a lower activation energy than from either $Si-H_2$ or $Si-H$ centers.

We have not calculated the vibrational structure of the three-center bonds proposed herein. There have been problems with unambiguous identification of the $2000 cm^{-1}$ infrared absorption with $Si-H$ centers and the $2090 cm^{-1}$ absorption with $Si-H_2$ centers.[20] It is important to consider the additional infrared absorption from three-center bonds before such problems can be fully resolved.

IV. Acknowledgments

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+Department of Electrical Engineering and Computer Science.

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Figure Captions

Figure 1: SCF-Xα-SW molecular-orbital energy levels of an $Si_2(sat)_6$ cluster having the following configurations:

A. Staggered conformation with Si-Si distance = 2.35$\overset{o}{A}$

B. Eclipsed conformation with Si-Si distance = 2.35$\overset{o}{A}$

C. Staggered conformation with Si-Si distance = 3.2$\overset{o}{A}$

The highest occupied molecular orbitals are indicated by arrows, and orbitals with appreciable density between Si atoms are shown as solid lines.

Figure 2: Bond types for the formation of a $Si_2(sat)_6H_2$ complex. Vertical lines denote nodes and horizontal lines indicate bonding.

Figure 3: SCF-Xα-SW molecular-orbital energy levels of an $Si_2(sat)_6H_2$ complex as a function of H-H distance, with the Si-Si distance held at 3.2$\overset{o}{A}$.

A. Staggered conformation of $Si_2(sat)_6$ cluster shown for comparison (same as Figure 1C).

B. H-H distance = 0.53$\overset{o}{A}$

C. H-H distance = 0.80$\overset{o}{A}$

D. H-H distance = 1.00$\overset{o}{A}$

The highest occupied molecular orbitals are indicated by arrows, and orbitals with appreciable density between Si atoms are shown as solid lines.

Figure 4: Contour map for the $Si_2(sat)_6H_2$ molecular-orbital wave function of lowest energy in Figure 3C. This orbital is bonding between the hydrogen atoms.

Figure 5: Contour map for the $Si_2(sat)_6H_2$ molecular-orbital wave function of second-lowest energy in Figure 3C. The solid and dashed contours represent positive and negative vaues, respectively, of the wave function. This orbital is bonding between the hydrogen atoms.

Figure 6: Contour map for the $Si_2(sat)_6H_2$ molecular-orbital wave function of third-lowest energy in Figure 3C. The solid and dashed contours represent positive and negative values, respectively, of the wave function. This orbital is <u>antibonding</u> between the hydrogen atoms.

Figure 7: Contour map for the $Si_2(sat)_6H_2$ molecular-orbital wave function of fourth-lowest energy in Figure 3C. The solid and dashed contours represent positive and negative values, respectively, of the wave function. This orbital is antibonding between the hydrogen atoms.

Figure 8: SCF-$X\alpha$-SW molecular-orbital energy levels of an $Si_2(sat)_6H_2$ complex as a function of Si-Si distance and H_2 molecular orientation, with the H-H and Si-H distances held at $0.8\overset{o}{A}$ and $1.35\overset{o}{A}$, respectively.

A. Si-Si distance = $3.4\overset{o}{A}$
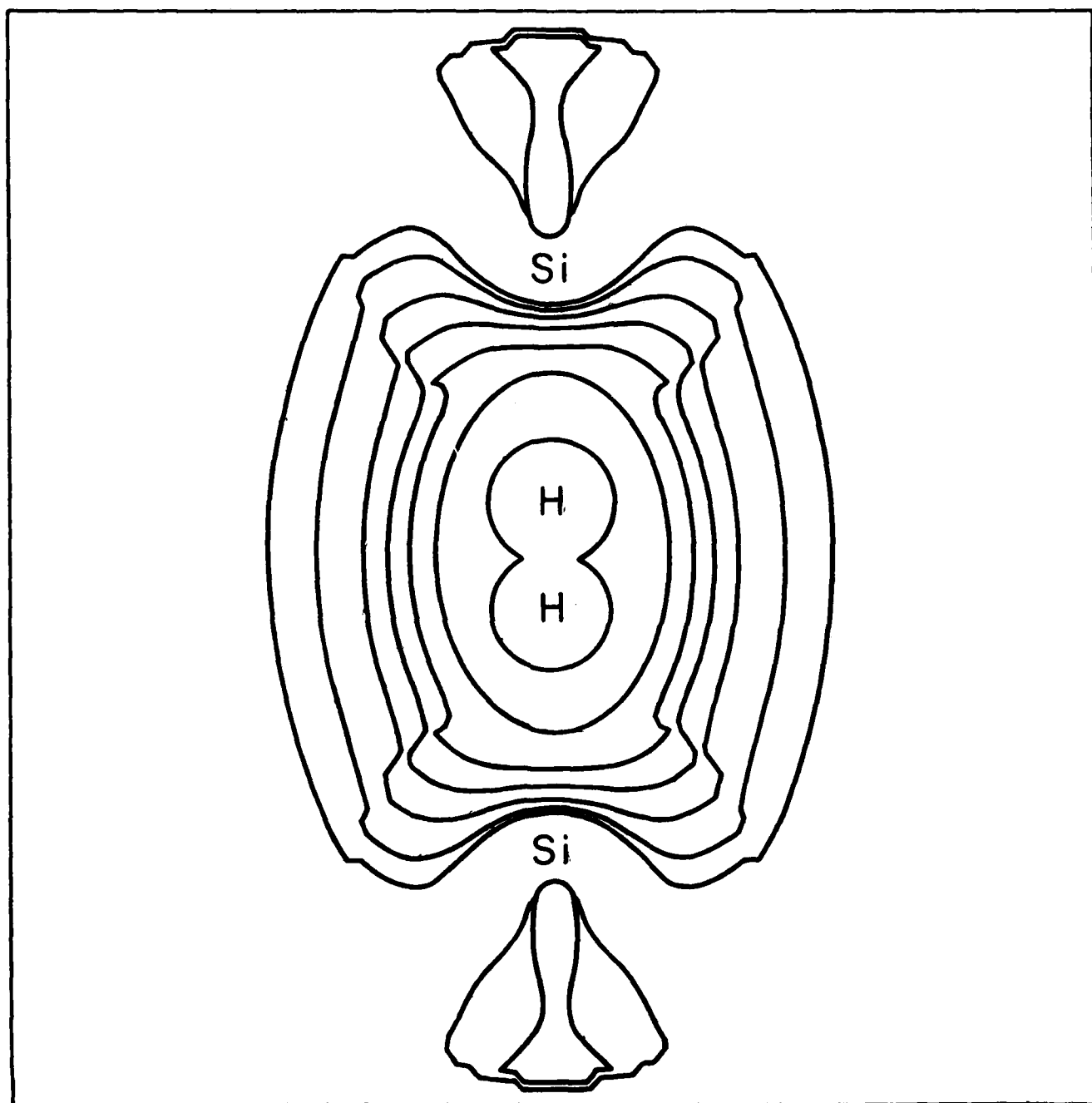
B. Si-Si distance = $3.2\overset{o}{A}$
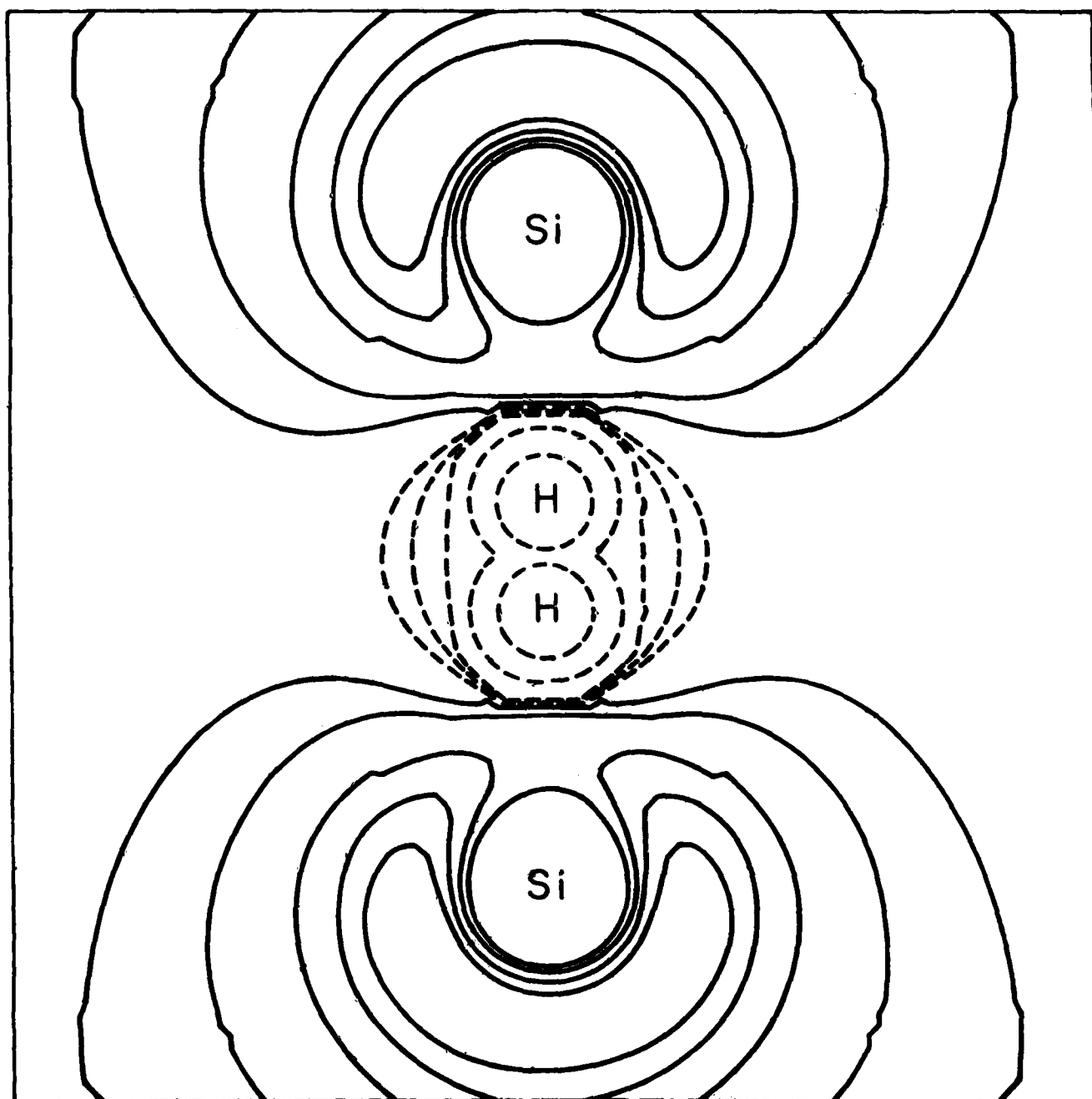
C. Si-Si distance = $2.5\overset{o}{A}$

The highest occupied molecular orbitals are indicated by arrows, and orbitals with appreciable density between Si atoms are shown as solid lines.
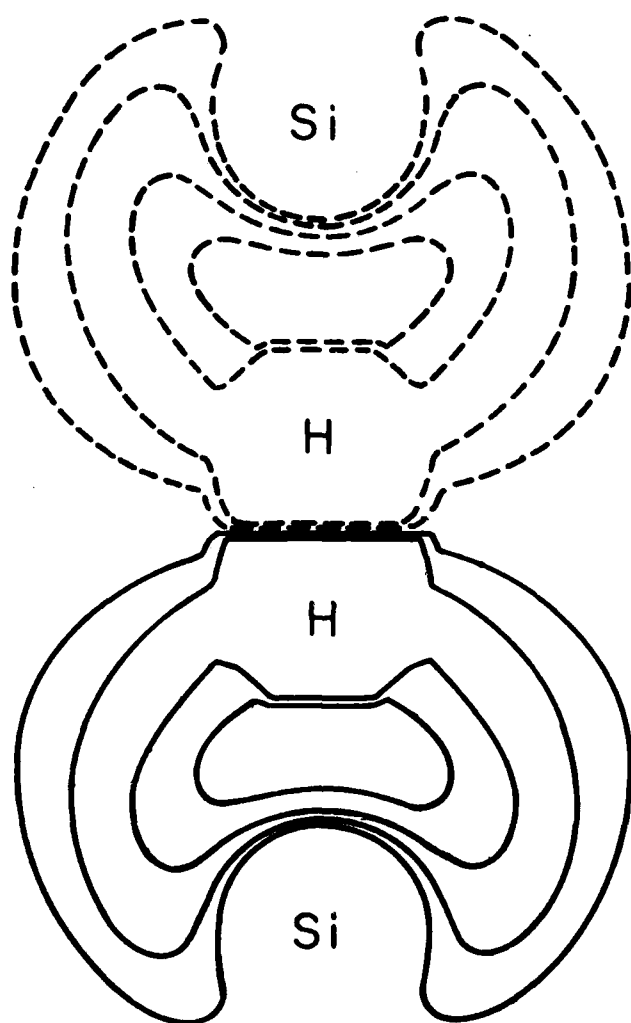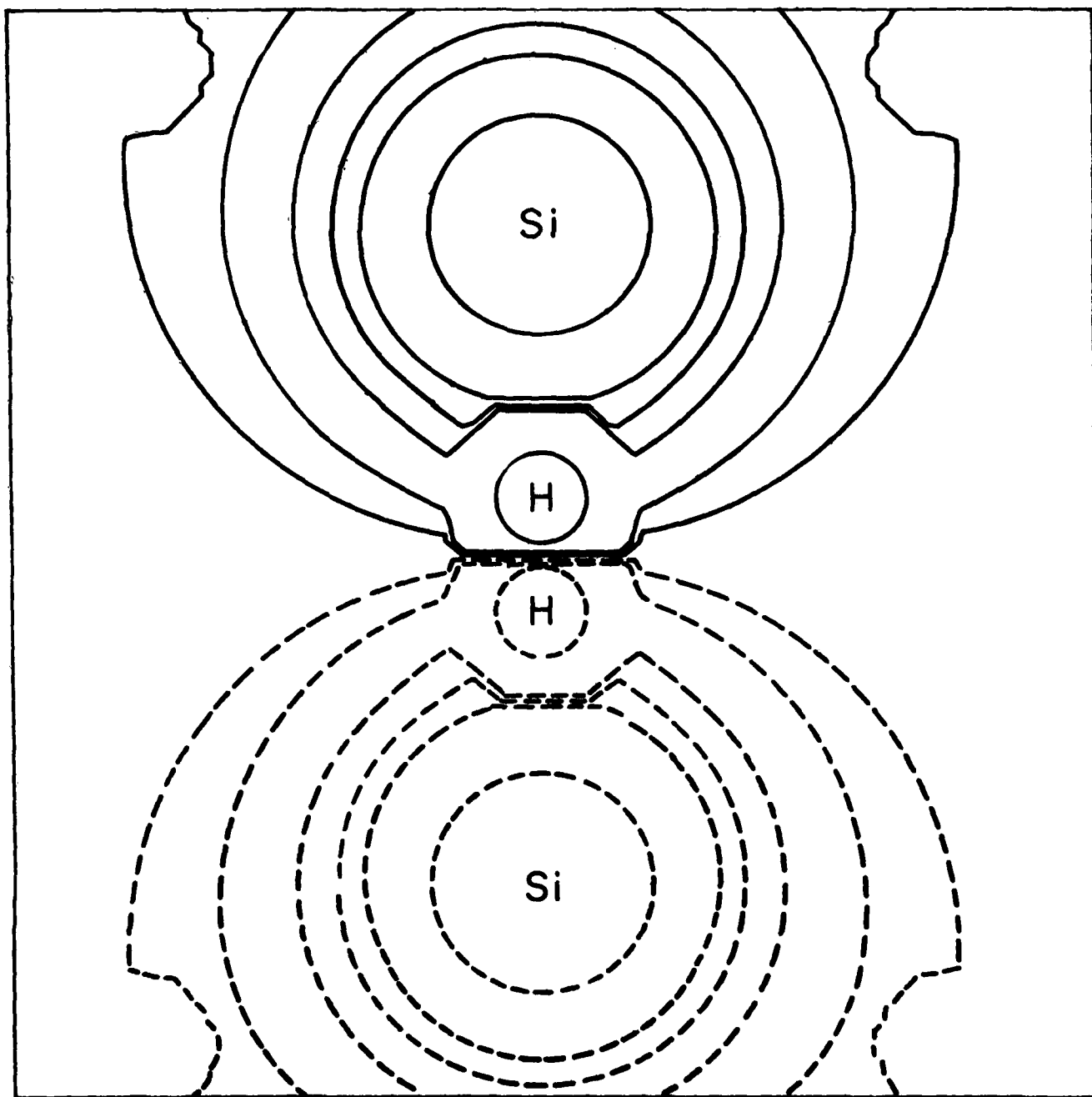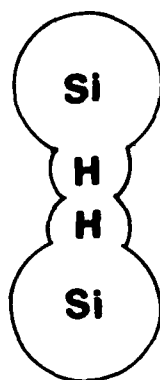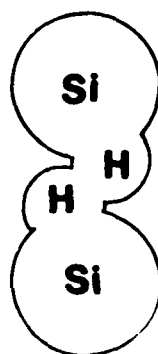
Figure 9: SCF-$X\alpha$-SW molecular-orbital wave function of lowest energy in Figure 8B. The solid and dashed contours represent positive and negative values, respectively, of the wave function. This orbital is <u>bonding</u> between the hydrogen atoms.

Figure 10: SCF-$X\alpha$-SW molecular-orbital energy levels of an $Si_2(sat)_6H$ complex as a function of the position of the H atom between the Si atoms, with the Si-Si distance held at $3.2\overset{o}{A}$.

A. Si-H distance = $1.6\overset{o}{A}$

B. Si-H distance = $1.34\overset{o}{A}$

C. Si-H distance = $1.2\overset{o}{A}$

D. Si-H distance - $1.07\overset{o}{A}$

The highest occupied molecular orbitals are indicated by arrows, and orbitals with appreciable density between Si atoms are shown as solid lines.

H

H—H

H—H

H

Si—H—H—Si
Type 4

Si—H—H—Si
Type 3

Si—H—H—Si
Type 2

Si—H—H—Si
Type 1

Si(ent)₃

(ent)₃Si—Si(ent)₃

(ent)₃Si—Si(ent)₃

Si(ent)₃

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